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Molecular population of vibrational states of carbon dioxide

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The molecular population of the vibrational states of carbon dioxide has been calculated in the temperature range 300–2000 K. The calculations show that at higher temperatures the molecules are excited predominantly to the fundamental bending mode and its overtones.

1. Introduction

Carbon dioxide is a linear, symmetric, triatomic molecule, in which the atoms lie in a straight line. This molecule can vibrate in three different fundamental modes which can be described as symmetric stretching, antisymmetric stretching and bending. The vibrational energy levels are normally designated by three numbers representing the number of vibrational quanta of each mode associated with the level and written in the order v_1, v_2 and v_3.

Vucelic *et al* (1973) have carried out *ab initio* calculation of the vibrational and electronic properties of CO_2. On the basis of the vibrational frequencies given by them, it is possible to compute the molecular population of various vibrational states of CO_2 as a function of temperature.

This knowledge of the molecular population is particularly useful in the study of the vibrational energy diffusion coefficients for the various modes at different temperatures (Chen *et al* 1975). In this respect, CO_2 molecule provides an interesting study, since it has been estimated that with increasing temperatures as much as about 40 per cent contribution to its total thermal conductivity comes from vibrational states (Chen *et al* 1975).

2. Theory

The basis of the computation of the molecular population is as follows.

The number, N_v, of the molecules in a state, v at a temperature, T, is given by the Boltzmann's expression (Wilson *et al* 1955):

$$N_v = N_0 . e^{-(E_v - E_0)/kT}. \quad \ldots (1)$$

Here,

N_0 = Number of molecules in the ground state (000),
E_v = Energy in the state v,
E_0 = Energy in the ground state (000),
k = Boltzmann's constant.

Now the total number of molecules, N, is given as :

$$N = \sum_{v=0}^{\infty} N_v = N_0 \sum_{v=0}^{\infty} e^{-(E_v - E_0)/kT}$$

$$= N_0 Q \qquad \ldots (2)$$

where Q is the Partition Function.

Hence combining eqs. (1) and (2), we get,

$$N_v = \frac{N}{Q} \cdot e^{-(E_v - E_0)/kT}$$

or,

$$\frac{N_v}{N} = \frac{1}{Q} \cdot e^{-(E_v - E_0)/kT} \qquad \ldots (3)$$

Also from Bohr's frequency rule (Johnson 1949), it is known that,

$$E_v - E_0 = hc\bar{\nu} \qquad \ldots (4)$$

where h is the Planck's constant, c is the velocity of light and $\bar{\nu}$ is the wave number corresponding to the transition between the energy levels E_v and E_0.

The eq. (3) can, therefore, be rewritten as,

$$\frac{N_v}{N} = \frac{1}{Q} \cdot e^{-hc\bar{\nu}/kT} \qquad \ldots (5)$$

Thus, the fraction of the molecules in a particular state v can be calculated from eq. (5).

3. Results and Discussion

The computed values of $hc\bar{\nu}$ for various vibrational states are given in the Table 1, the corresponding values of $\bar{\nu}$ being taken from Vucelic *et al* (1973). The population of the molecules, computed from eq. (5), in the various vibrational states is displayed graphically in Fig. 1 as a function of temperature.

Table 1. Values of $\bar{\nu}$ and $hc\bar{\nu}$ for various vibrational states of CO_2 with respect to the ground state (000)

Vibrational State	$\bar{\nu}$ cm^{-1}	$hc\bar{\nu}$ $erg \times 10^{14}$
100	1420	28·20
200	2840	56·40
300	4260	84·60
010	679	13·48
020	1358	26·97
030	2037	40·46
040	2716	53·94
001	2429	48·24

From the Fig. 1, it can be seen that the population of the ground state molecules goes on decreasing with temperature until it reaches 32% at 2000K, and near the room temperature, the vibrationally excited molecules are only in the (010) mode. Further, in the temperature range 1100–2000K, about 36 to 44% of the molecules are excited to the fundamental bending mode (010) and

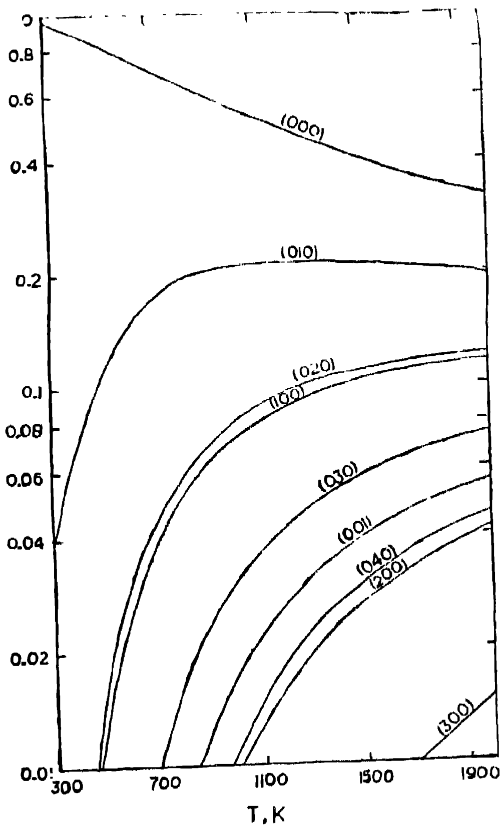

Fig. 1. Molecular population of CO_2 at different vibrational levels as a function of temperature.

its overtones (020), (030) and (040). For the same temperature range, the molecules in the fundamental symmetric mode (100) and its overtones (200, 300) are 9·5 to 17% while the molecules in the fundamental asymmetric mode (001) are only 3·1 to 5·6%. Another interesting observation is that the population of the (010) mode remains almost constant at nearly 20% from 900 to 2000K and that of all the other levels always remains below 12%.

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